METHOD FOR PREPARATION OF CHEMICALLY CROSSLINKED POLYACRYLONITRILE POLYMER ELECTROLYTE AS SEPARATOR FOR SECONDARY BATTERY

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to chemically crosslinked polyacrylonitrile (PAN) polymer electrolytes, and more particularly to polymer electrolytes as separator between positive and negative electrode for secondary battery. This crosslinked polyacrylonitrile polymer electrolyte consists of polyacrylonitrile gel-type electrolytes, polyvinylidene fluoride (PVdF) and liquid electrolytes.

[0003] 2. Description of the Prior Art

[0004] Advances in electronic products are rapid in the recent years. The electronic product that are portable such as notebook, cell phone, PDA, and digital recorder are getting lighter and cheaper. According to enormous consumer market, the battery industry including nickel-cadmium battery, nickel-hydrogen battery, and lithium battery is developed and advanced fleetly. The battery size is smaller, capacity is higher than conventional one, besides, battery materials are compatible to the environment.

[0005] In early 1990, Japan has succeeded in commercializing lithium ion battery. In the lithium ion battery, the positive electrodes are $LiMnO_2$, $LiMn_2O_4$, $LiCoO_2$, $LiNiO_2$ crystal powder, the negative electrodes are graphite or irregularly crystal carbon, and the separator is made of porous PP membrane or nonwoven fabrics. The separator filling with electrolytes, i.e., non-aqueous lithium salt, serves as an ionic conducting bridge. In the charge process, lithium ion moves from crystal lattice of the positive electrode to electrolytes, and then lithium ion in the electrolytes solution is moved into crystal lattice of the negative electrode. The mechanism of discharge process is reverse to that of the charge process.

[0006] The lithium battery (a secondary battery) has the advantages of high capacity, high voltage and high density; moreover, its size has potential to be minimized. Because the liquid electrolytes possibly may leak out, it must seal lithium battery closely via metal shell. Thus, it may limit lithium battery to be minimized. To overcome the leaking of the liquid electrolytes, the polymer electrolyte lithium battery is developed.

[0007] The polymer electrolyte lithium battery substitutes a separator of the conventional lithium secondary battery for the polymer electrolyte separator that can absorb liquid electrolytes to eliminate the problem of electrolytes leaking. Moreover, the adhesive property of the polymer electrolyte membrane can closely be compacted to positive and negative electrode, and also tend to simplify battery manufactures.

[0008] Armand et al. (U.S. Pat. No. 4,303,748, 1981) provided solid polymer electrolyte membrane instead of the liquid electrolyte for batteries. The solid polymer membrane consists of polymers and lithium salts. At that time, the polymer membrane was made of PEO, PPO, electrolytes salts of alkaline-metal and alkaline-earth group. Although the solid polymer electrolyte membrane has strong mechanical strength, its conductivity at room temperature is relatively low and hereby not easy to be used wildly in the battery product. After several researchers striving, the problem of low conductivity at room temperature still exits ("Polymer Electrolytes", Fiona M. Gray, 1997, pages 37-44).

[0009] To improve the low conductivity, someone tried to add plasticizers into polymer to increase electrolyte membrane conductivity. The polymer electrolytes containing liquid electrolytes different from solid polymer electrolytes are called gel-type polymer electrolytes. Chua et al. (U.S. Pat. No. 5,240,790, 1993) mixed PAN polymer with γ-butyrolactone and lithium salts to form electrolytes, which was similar to liquid electrolytes in conductivity. But the gel-type polymer electrolyte membrane will become soft above 50° C. for long time because of its weak mechanical strength.

[0010] Luying Sun et al. from American Battery Engineering (U.S. Pat. No. 5,609,974, 1997) provided a chemically crosslinked gel-type electrolytes that mixed three monomer, which were PAN, 2-ethoxyethyl acrylate, and tri(ethylene glycol) dimethacrylate, with liquid electrolytes, and then added AIBN as an initiator finally, formed above mixture to a membrane and polymerized by heating. The chemically crosslinked gel-type electrolytes improved PAN electrolytes's defect, that is, it would be soft at high temperature, but must use cellulose filler to enhance mechanical strength. Moreover, the solution was not suitable for forming a membrane due to the low viscosity, and it would cause inefficiently compact to a positive and a negative electrode, which resulted in hardly producing battery automatically.

[0011] Gozdz et. al. from Bell Communications Research Company provided porous gel-type electrolyte membrane based on PVdF polymer to achieve higher conductivity and mechanical strength. However, the electrolytes' absorbability of polymer electrolyte membrane will decrease at high temperature, and the complex manufacture processes of membranes were not suitable for the industry.

[0012] Amano et al. form Japan NEC Company (U.S. Pat. No. 6,235,433, 2001) added PVdF into pre-polymerizing solution of crosslinked gel-type acrylic electrolytes through forming membrane and finally crosslinked-polymerized by heating. This method announced it could make the electrolyte membrane have advantages of well mechanical strength of PVdF electrolytes membrane and superior electrolytes absorbability of gel-type acrylic electrolytes. However, the solubility parameter (δ) of acrylic polymer is only 9~10, which is far from ethylene carbonate (EC) and propylene carbonate (PC) those values of δ are 14.7 and 13.3, respectively, and causes low conductivity due to weak the absorbability. In addition, the liquid electrolytes would be withdrawn from the electrolyte membrane if it were used a long time.

[0013] The solubility parameter of PAN polymer is 15.4, that is similar to EC and PC solvent. The electrolytemembrane conductivity will rise to 4×10^{-3} S/cm or above when PAN polymer is used as membrane. (B. Scrosati, Chem, Mater. Vol. 538, page 6, 1994)

[0014] Eventually, the prior-art mentioned above has following disadvantages:

[0015] 1 Since lithium secondary batteries in which liquid electrolytes may leak outside, and it must be seal closely by metal shell.